CEMENT
AND
CEMENT MANUFACTURE

PUBLISHED 20TH OF EACH MONTH. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 12s. POST FREE.

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED,
20, DARTMOUTH STREET, LONDON, S.W.1.
TELEPHONE: WHITEHALL 4551.
TELEGRAPHIC ADDRESS:
CONCRETIUS, PARL, LONDON.

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & CEMENT MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME 8. NUMBER 4. APRIL 1935.

Heat Transmission in Rotary Kilns.—XI.

By W. GILBERT, Wh.Sc., M.Inst.C.E.

Estimation of the Charge in the Kiln.

(236) It was shown in Parts IX and X of this series of articles* that the highest rate of heat transmission will be obtained by using a relatively large charge in the decomposition zone and a relatively small charge in the earlier stages of the drying zone. In a normal rotary kiln, however, the size of the charge in each stage is not usually predetermined, and it tends to become large throughout the drying zone and small in the decomposition zone.

The charge area at any cross section of the kiln can be calculated by

$$W \times A \times M = Q \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where W = weight of clinker constituents in lb. per cubic foot of charge,
A = area of charge in cross section in square feet,
M = movement of charge down kiln per minute in feet, and
Q = clinker output in lb. per minute.

The value of M can be obtained from Table XXX (see Part IX) as soon as the slurry has formed into small lumps and become dry on the surface.

(237) As an example, the charge volume per cent. has been calculated for Stages (4) to (11) of the 400-ft. kiln (as illustrated in Fig. 19, Part VI†), and the result is shown in Table XXXVII. The figures in col. (4) are based on a charge advance of 22.1 per cent. of the stage diameter per revolution. The composition of the slurry entering the kiln was 151.6 lb. of raw material (corresponding to 100 lb. of clinker) to 112 lb. of water. The figures in col. (5) are based on a raw material density reckoned solid of 166 lb. per cubic foot. It is assumed that the lump dimensions would not shrink in drying after the moisture had been reduced

* Cement and Cement Manufacture, July and October, 1934.
† Cement and Cement Manufacture, December, 1933.

TABLE XXXVII.

SHOWING THE CHARGE PER CENT. IN VARIOUS STAGES OF THE 400-FT. KILN AS CALCULATED.
Advance of charge per kiln revolution (or per minute) 0.221 D.

Stage number.	Stage diameter in feet. D.	Stage area in cross section. sq. ft.	Advance of charge per kiln revolution. feet.	Weight of dry material per cu. ft. of charge. lb.	Weight of clinker per cu. ft. of charge. lb.	Charge area in cross section. sq. ft.	Charge per cent.	Object of stage.
4	8.37	55.0	1.85	67.0	44.2	7.07	12.8	Drying raw material, 3rd quarter.
5	8.20	52.8	1.81	79.0	52.1	6.10	11.6	,, ,, ,, 4th quarter.
6	8.20	52.8	1.81	79.0	52.1	6.10	11.6	Raising 212–451 deg.
7	9.00	63.6	1.99	79.0	52.1	5.56	8.8	Raw 451–690 deg.
8	10.20	81.7	2.25	79.0	52.1	4.92	6.0	material 690–995 deg.
9	10.20	81.7	2.25	79.0	52.1	4.92	6.0	temperature 995–1,300 deg.
10	10.20	81.7	2.25	72.0	52.1	4.92	6.0	Decomposing $CaCO_3$, first half.
11	10.20	81.7	2.25	59.0	52.1	4.92	6.0	,, ,, second half.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

to 15 per cent. by weight (or 32 per cent. by volume) since the exterior would then be dry and hard. Taking the volume of the interstices between the lumps to be 30 per cent. of the charge volume, it follows that the weight of 1 cubic foot of dry material in Stages (5) to (9) is $166 \times 0.68 \times 0.70 = 79$ lb. The weight of the clinker constituents per cubic foot of charge is $79 \times 100 \div 151.6 = 52.1$ lb., as shown in col. (6). The lump dimensions are assumed to remain unaltered throughout the decomposition zone, hence the weight of the clinker constituents per cubic foot of charge will be the same as in Stages (5) to (9). The charge area in col. (7) is calculated by formula (8). $Q = 578.5$.

Re-arrangement of Kiln to give Charge Desired in Each Stage.

(238) It is seen from col. (8) that the charge in Stage (4) is 12.8 per cent., and the charge in Stage (3) would probably be greater. On the other hand, the charge in the decomposition zone is only 6 per cent. This is the reverse of what is required, hence a somewhat important problem is presented for solution. Since kilns are now built up to 500 ft. in length it is suggested that they should be divided into two parts, preferably at the end of the drying zone which is at, or near, 70 per cent. of the kiln length [see Fig. 28 in Part VIII, May, 1934]. Other particulars would be: Drying zone, slope 1 in 25, speed 1.5 R.M.P.; Decomposition zone, slope 1 in 75, speed 1 R.P.M.

Calculation shows that as the lining speed is reduced the efficiency of the heat transmission between the lining and the underside of the charge falls off, hence it may prove better to reduce the slope of the decomposition zone than to reduce the speed. It is possible that an increase of charge from 6 per cent. to 20 per cent. in the decomposition zone would not only substantially increase the rate of heat transmission but would produce better clinker.

Verification of Assumptions Made.

(239) Before concluding these articles it is considered desirable to verify two of the earlier assumptions made, which are (*a*) That the average surface temperature of the raw material lumps will remain at or near 212 deg. F. until all the moisture is evaporated. The calculations for the length of the drying zone, which is the major part of the kiln, are based on this assumption. (*b*) That the rise of the lump surface temperature when resting on the kiln lining in Stages (6) to (12) is sufficiently allowed for by using the rather low absorption factor of 0.75, see Part III (June, 1933), para. (52). The length calculated for the decomposition zone is here in question. To clear up these items it is necessary to take into account the circulation of the charge in the kiln, the length of the heating cycle, and the size of the individual lumps.

(240) The Circulation of the Charge in the Kiln.—A study is first made of the manner in which the component particles of the charge are circulated during each revolution of the kiln. A model of the simplest kind is used, consisting of a glass jam jar lined on the circumference inside with emery cloth and charged with standard sand. Fig. 43 shows the lower end of the jar with the charge ABK. If the jar is rolled along a level surface it will be seen from the end view that owing to the relatively low speed the charge does not circulate within itself as

the balls in a tube mill may be seen to do, but all the particles turn with the jar until the line AB (which is approximately the natural slope of the sand) is reached and the material then falls down the chord BA. A sand particle, for instance, starting at D will traverse the arc DFE and on reaching E it may be assumed to fall to D where the cycle is completed. Since the time taken by the sand to fall from E to D in a rotary kiln is negligible when compared with the time required to traverse the arc DFE, the number of cycles per kiln revolution will be $\frac{360}{\phi}$ very nearly, where ϕ is the angle subtended by DE at the centre of the circle.

(241) Particles which travel along the lining arc AKB, and fall from B to A, will obviously go through a less number of cycles per kiln revolution. Suppose the whole of the charge area ABK to be divided into a number of concentric strips, and let the area of each strip be multiplied by the number of cycles which the material assumed to traverse it makes per kiln revolution. On adding the

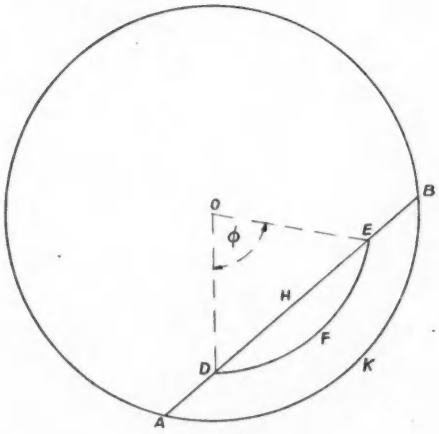


Fig. 43.

product for each strip and dividing by the area of the charge an average value is obtained for the number of times each particle of the charge is circulated per kiln revolution. The result may be obtained graphically for any charge, or it may be taken from the formula

$$tN = \frac{0.0987\ K^2}{C} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

where tN = number of complete turns of the charge per kiln revolution,
K = chord length per cent. circumference, from Table XXXI, Part X (October, 1934), and C = charge per cent.

Taking for example a charge of 8 per cent., $tN = \frac{0.0987 \times (21.69)^2}{8} = 5.81$.

Values of tN for charges up to 25 per cent are shown below :

Charge per cent.	5	8	13	20	25
Value of tN	7.02	5.81	4.70	3.79	3.35

It is seen that the charge is turned completely over several times per kiln revolution.

(242) ADVANCE OF THE CHARGE.—A further study of paras. (240) and (241) showed that the charge advance per kiln revolution could be calculated. A formula was obtained,

$$M.p.d. = \frac{0.207\,K^3}{C\,L\sin\theta} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where $M.p.d.$ = Movement of charge down kiln per revolution, per cent. diameter,
L = ratio of kiln length to rise, and
θ = slope of surface of charge in degrees.
K and C are defined in para. (241).

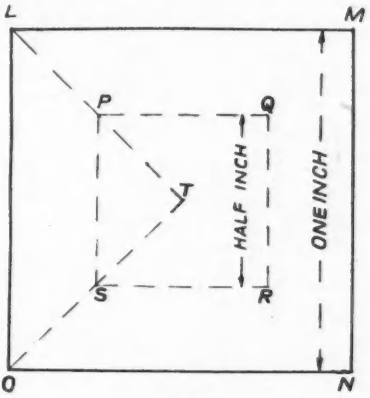


Fig. 45.

Formula (10) gives a somewhat slower rate of advance than that shown in Table XXX, Part IX, especially when a large charge is used ; it is therefore desirable to verify it in practice when opportunity occurs.

When deriving formula (10) it became clear that the movement of the charge down the kiln would not be appreciably affected by irregularities in the lining, since the advance takes place as the material falls down the chord.

Reference to Experiments on Clay Drying.

(243) To illustrate the position with regard to the surface temperature of the material in the drying zone [see para. (239) (*a*)] reference is made, by permission of Messrs. Edgar Allen & Co., Ltd., to some experiments on the drying of clay. In a typical experiment some of the clay was moulded into a cube of 1 in. side,

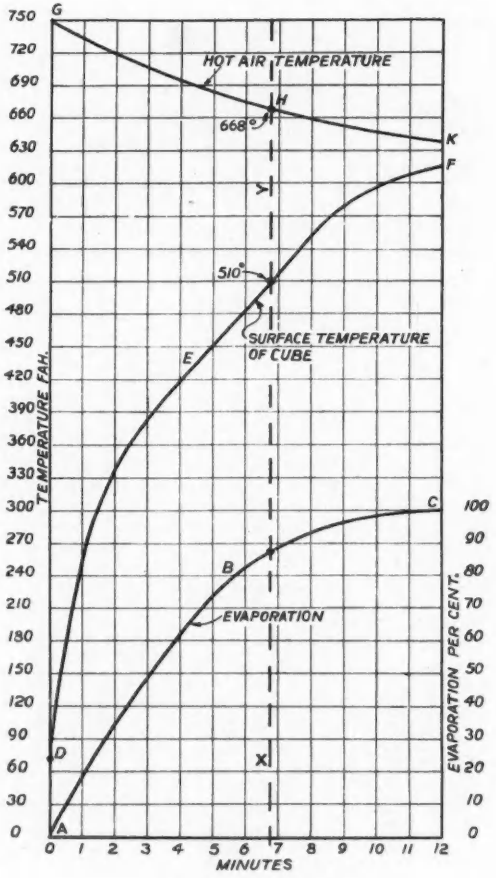

HOT AIR TEMPERATURE
668°
510°
SURFACE TEMPERATURE OF CUBE
EVAPORATION
TEMPERATURE FAH.
EVAPORATION PER CENT.
MINUTES
G
H
K
F
E
C
B
D
A
X
Y

Fig. 44.

placed on a wire grid, and fully exposed to a current of hot air at a temperature of 750 deg. F. and a velocity of 24 ft. per second. The initial moisture in the clay was 30.5 per cent.

The result of the experiment is shown in Fig. 44, where the base line represents time in minutes. The proportion of moisture evaporated at any instant is given by the curve ABC and by the scale on the right. The average surface temperature of the cube throughout the experiment was measured indirectly ; it is shown by curve DEF. Allowing for the heat lost by radiation from the surface of the cube the hot air temperature available for drying is shown by curve GHK. The rate of heat transfer between the hot air and the surface of the cube averaged 14.6 B.T.U. per square foot per hour per deg. Fah.

(244) Taking for example the ordinate $X\ Y$ at 6¾ minutes, the evaporation is 0.875, or seven-eighths of the total, hence one-eighth of the original moisture remains. The hot air temperature is 668 deg. F., and the cube surface temperature 510 deg. F. For calculation purposes it is assumed that the residual moisture will be contained by an inner cube $P\ Q\ R\ S$ (Fig. 45) whose volume is one-eighth that of the original cube LMNO of 1-in. side. The side of the inner cube is therefore ½ in.

After the surface moisture has been removed by the hot air evaporation is assumed to take place at 212 deg. F. ; hence the temperature difference available for moving the heat supply from the face of the outer cube to the face of the inner cube, across the dry material, at the ordinate $X\ Y$ is $510 - 212 = 298$ deg. F. Similarly the temperature difference available for transferring the heat from the hot air to the cube surface is $668 - 510 = 158$ deg. F. A balance is thus set up : heat is supplied by the hot air to the cube surfaces by convection as rapidly as it can be conducted through the dry material to the surface of the inner cube.

From the figures given it is estimated that the conductivity K of the dry clay at this point is 3 B.T.U. per sq. ft. per hour per deg. Fah. per inch of thickness.

(245) It is important to notice the rapid rise of the surface temperature at the beginning of the experiment. When seven-eighths of the moisture has been evaporated the temperature difference available for drying is only 158 deg. F., but if the lump surface temperature remained throughout the experiment at 212 deg. F., as it is assumed to do in the drying zone of a rotary kiln, a temperature difference of $750 - 212 = 538$ deg. F. would be available, or more than three times as much. It remains therefore to consider in some detail the drying and heating processes in a rotary kiln in order to find out to what extent the rise of the surface temperature of individual lumps is likely to interfere with the supply of heat to them.

Drying in Stage (5) of the 400 ft. Kiln.

(246) The drying conditions are examined at the centre of Stage (5) of the 400-ft. kiln [see Fig. 19, Part VI, December 1933]. Stage (5) has a length of about 36 ft., and in it the last quarter of the slurry moisture is evaporated. The charge is now taken at 9.5 per cent. (instead of 6 per cent.) and the diameter is increased

from 8.2 to 8.36 ft. in order to retain the same area of gasway. Further particulars are given in Appendix I.

For calculation purposes the material lumps are treated as cubes. They are assumed to circulate freely, as the lumps of raw material actually do.

(247) HEATING CYCLE PERIOD. In the kiln stages where the material is dry on the surface each lump will pass through a series of heating cycles. A heating cycle period is defined as the length of time required for all the cubes of the charge to be heated once on the lining of the lower arc. To trace a heating cycle we may assume a cube to start at *A*, Fig. 43, and to travel on the lining through the arc *AKB*; it then falls down part of the chord, and next traverses an arc

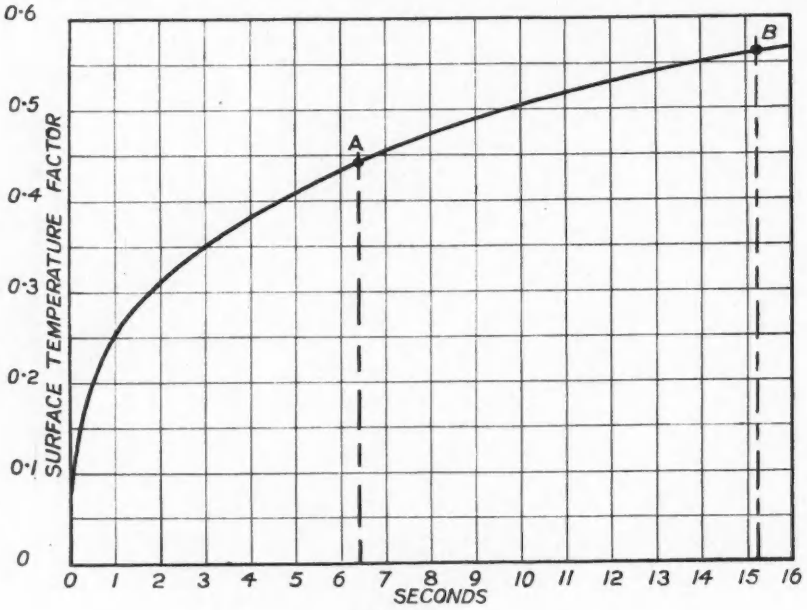


Fig. 46.

such as *DFE*. The movement continues until the cube has (under average conditions) passed over the entire charge area *AKB*. It then returns to point *A* and the heating cycle is complete.

A formula which gives the length of the heating cycle for cubes of any size is given in Appendix II. The result for a selection of cube sizes is given in Table XXXVIII, col. (2).

It is seen, for instance, that a cube of 1-in. side will pass through a complete heating cycle in 1.67 minutes. Of this period 0.254 minute is spent on the lower lining arc and 0.228 minute on the chord, the latter period representing nine journeys as deduced from formula (9).

TABLE XXXVIII

HEATING CONDITIONS AT THE CENTRE OF STAGE (5) FOR MATERIAL LUMPS OF VARIOUS SIZES.
Time on lower arc 0.254 minutes, time on chord 0.228 minutes, for all heating cycles.

Line number.	Side of cube. In.	Period of heating cycle (minutes).		Number of journeys down chord per cube cycle.	Rise of average surface temperature on lining, per cent. *Td*.	Average lump loss during the diffusion period, deg. Fah.	Lump loss at end of cycle, deg. Fah.	Heat received per sq. ft. per cycle.		Average temperature of charge, deg. Fah.
		For one cube.	For one face of one cube.					On chord B.T.U.	On lower arc B.T.U.	
1	½	13.36	80.2	72	29.1	3	2	95.0	74.5	214
2	¼	6.68	40.1	36	40.2	9	6	98.2	65.4	218
3	⅛	3.34	20.0	18	43.5	36	24	99.2	61.5	233
4	1	1.67	10.0	9	44.1	144	101	98.9	58.0	290
5	1½	1.11	6.7	6	44.1	325	251	97.3	51.9	381
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

A cube of $\frac{1}{8}$-in. side passes through a complete cycle in 13.36 minutes; of this period 0.254 minute is again spent on the lining and 0.228 minute on the chord. The latter period is spread over 72 journeys, but the $\frac{1}{8}$-in. cube would be mainly submerged and only exposed on the surface for a small part of each journey.

(248) SOME ASSUMPTIONS MADE.—In the calculations which follow the charge of $9\frac{1}{2}$ per cent. is assumed to consist of cubes of 1-in. side. Since one-eighth of the original moisture remains it is assumed to be contained by an inner cube of

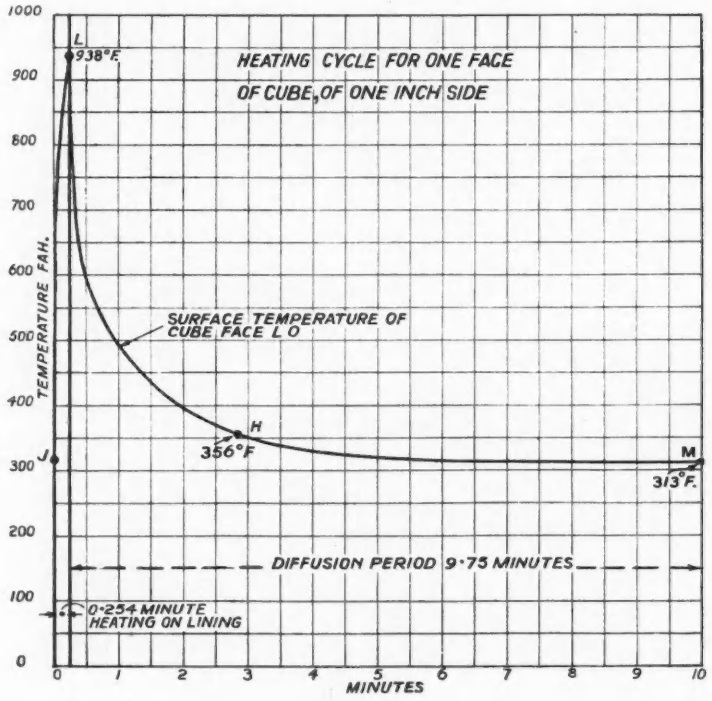


Fig. 47.

$\frac{1}{2}$-in. side; actually the inner cube would probably be somewhat larger, but the assumption is on the safe side. It is further assumed that each face of a cube comes on to the kiln lining in succession so that the face LO for instance (Fig. 45) will only be heated from the lining once every six cycles. The length of a heating cycle for any one face of a cube is given in Table XXXVIII, col. (3). Again each of the six pyramids forming the cube are assumed to be insulated from one another as regards heat transmission, so that all the heat received by the face LO will diffuse through the frustum LPSO and evaporate moisture at the face PS where

the temperature is 212 deg. F. It will be seen later that the assumptions made are reasonable.

The temperature difference between the face LO and the face PS is termed the " lump loss " and the values subsequently found for cubes of each size are entered in cols. (6) and (7) of Table XXXVIII.

(249) HEATING OF ONE FACE OF THE CUBE ON THE KILN LINING.—Starting at point A in Fig. 43 the face LO is heated on the lining for 0.254 minute, or 15.24 seconds. The corresponding rise of the surface temperature is shown by Fig. 46. After 15.24 seconds the surface temperature factor is seen to be 0.562, which means that the surface temperature has risen 56.2 per cent. of the initial temperature difference whatever that may be. In this case the face LO due to previous heating, comes on to the lining at a temperature of 313 deg. F.; the lining temperature is 1,425 deg. F.; hence the initial temperature difference is 1,112 deg. F. The rise of the surface temperature when on the lining is therefore $1{,}112 \times 0.562 = 625$ deg. F. and the final surface temperature is $625 + 313 = 938$ deg. F.

By measurement on the graph in Fig. 46 it is found that the average rise of the surface temperature during heating on the kiln lining is $0.441 \times$ (temperature difference)—see point A—hence the average surface temperature of the face LO during this period is $313 + (0.441 \times 1{,}112) = 803$ deg. F.

(250) The factor from which the average value of the surface temperature during the heating period on the lining is obtained is entered in col. (5) of Table XXXVIII for each size of cube. Its value depends on the density, specific heat, and conductivity of the material, and on the unit rate of heat transfer, but not on the actual temperature difference. The falling off in the value of the surface temperature factor for the smaller cubes is due to the reduced distance between the heated surface LO and the wet surface PS, see Fig. 45.

(251) THE DIFFUSION PERIOD.—Reference is now made to Fig. 47, the base line of which represents the length of a heating cycle for the face LO of a 1-in. cube. This is ten minutes [see Table XXXVIII, col. (3)]. The curve JL shows the temperature rise of the face LO during heating on the lining as obtained from Fig. 46 and the curve LHM shows the rapid fall in temperature of the same face during the diffusion period, which is the remainder of the cycle. During the latter period the heat stored in the frustum LPSO (Fig. 45) diffuses to the surface PS and is there used to evaporate the moisture.

During the diffusion period the charge is circulated 53 times, and the face LO receives heat " on chord " for a number of short periods of probably less than 0.5 second in duration, but which add up on the average to 0.228 minute [see para. (247)]. Due to heat received " on chord," and to its transfer across the frustum to evaporate the moisture, there will be a steady temperature difference of 101 deg. F. between the face LO and the face PS throughout the diffusion period.

Hence at point M on Fig. 47, although the heat received by the face LO on the lining has completely diffused to the face PS, there will be a lump loss of

313 − 212 = 101 deg. F. due to the heat which is being received "on chord." The average surface temperature of the face LO during the diffusion period, as measured on the graph, is 356 deg. F., hence the average lump loss during the diffusion period is 356 − 212 = 144 deg. F. The variation of the lump surface temperature throughout a heating cycle is further dealt with in Appendix III.

(252) AVERAGE CHARGE TEMPERATURE.—The average charge temperature for cubes of each size throughout a heating cycle is entered in col. (10) of Table XXXVIII. The average cube temperature at any instant is taken as half the sum of the temperatures of the two faces LO and PS in Fig. 45. Since most of the material will be in the form of rounded lumps of less than ½-in. in diameter

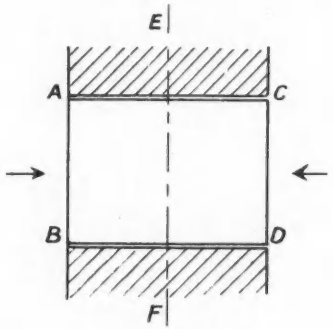


Fig. 48.

it is apparent that the average temperature of the charge in practice does not rise substantially above 212 deg. F. until the drying is nearly, or quite complete.

Heat Transmission per foot Run of Kiln.

(253) The lump losses for cubes of various sizes during a heating cycle having been calculated, the effect in each case is best seen by calculating the corresponding rate of heat transmission per foot run of kiln by the method previously used. A charge of 1-in. cubes is again taken by way of example. The data required are in Appendix I, lines (1) to (15). The relevant temperatures, together with the corresponding values for black body radiation and gas radiation, where required are shown below.

	Temperature, deg. Fah.	B.T.U. per square foot per minute.	
		Black body radiation.	Gas radiation.
(*a*) Gas	1,993	—	271.3
(*b*) Lining (circle)	1,425	364.8	112.1
(*c*) Material (on chord)	356	12.9	5.4
(*d*) ,, (on lower arc)	803	—	—

Line (*b*) The average lining temperature has to be assumed in the first instance. Its fluctuation during each revolution is neglected in the drying zone. Line (*c*) The average material temperature on chord is found by adding 212 deg. to the lump loss shown in col. (6) of Table XXXVIII. Line (*d*) This figure was derived in para. (249).

The various details of the heat transmission are worked out in the following. A condition is that the heat supplied to the kiln lining per minute must be equal to the heat which it gives out. The emission and absorption factors used in lines (1) (3) and (5) are those given in Table XXVI in Part VIII.

At the centre of Stage (5).	B.T.U. per foot run of kiln per minute.	
(1) Gas radiation to upper lining arc $(271.3 - 112.1) \times 0.8 \times 19.6$	2,497	
(2) Convection, gas to upper lining arc $(1,993 - 1425) \times \frac{1.98}{60} \times 19.6$	367	2,864
(3) Gas radiation to material chord $(271.3 - 5.4) \times 0.8 \times 5.98$	1,272	
(4) Convection, gas to material chord $(1,993 - 356) \times \frac{2.34}{60} \times 5.98$	382	1,654
(5) Upper lining arc, radiation to material chord $(364.8 - 112.1 - 12.9 + 5.4) \times 0.8 \times 0.8 \times 5.98$		939
(6) Lower lining arc, heat transfer to material $(1,425 - 803) \times \frac{22.0}{60} \times 6.66$		1,520
(7) Shell radiation loss		405
Total heat transmission		4,518

(254) Referring to line (6), the unit rate of heat transfer between the lower lining arc and the material is given in Appendix I, line (15). In Stage (5) the material is dry on the surface, and nearly the same result would be obtained if the heat transfer were assumed to be by radiation. Values of H_{con} for Stages (1) to (5) are given in Part VII, para. (137).

The heat received by the kiln lining per minute [see lines (1) and (2)] is 2,864 B.T.U. and the heat given out by the lining per minute is the sum of lines (5), (6) and (7), which is also 2,864 B.T.U. Hence the lining temperature assumed is suitable.

HEAT RECEIVED PER CYCLE "ON CHORD."—This quantity is required in order to calculate the lump loss during the diffusion period [see Appendix III, para. (261)]. From lines (3), (4) and (5) the heat transmitted to the material on the chord per square foot per minute is $\frac{2,593}{5.98} = 434$ B.T.U.

Since the material receives heat for 0.228 minute per heating cycle on chord, the quantity required is $434 \times 0.228 = 98.9$ B.T.U.

TABLE XXXIX.

STAGE (5).—EFFECT OF LUMP SIZE ON THE HEAT TRANSMITTED PER FOOT RUN OF KILN.

Line No.			Lump size zero. (1)	⅛-in. cubes. (2)	¼-in. cubes. (3)	½-in. cubes. (4)	1-in. cubes. (5)	1½-in. cubes. (6)
1	Heat transmitted per cent. on clinker		2.37	2.37	2.37	2.37	2.37	2.37
2	Average gas temperature .. .. .. deg. Fah.		1,993	1,993	1,993	1,993	1,993	1,993
3	Average lining temperature (for circle) .. ,,		1,238	1,346	1,390	1,407	1,425	1,457
4	Average material surface temperature (on chord) ,,		212	214	221	248	356	537
5	Average material surface temperature (on lower arc) ,,		212	543	689	745	803	901
6	Gas radiation to material chord	All heat quantities in lines (6) to (11) are in B.T.U. per foot run of kiln per minute.	1,286	1,285	1,285	1,284	1,272	1,242
7	Gas convection to material chord		415	414	412	407	382	339
8	Upper lining arc, radiation to chord		606	793	878	912	939	972
9	Lower lining arc to material		2,510	1,958	1,713	1,614	1,520	1,362
10	Shell radiation loss		405	405	405	405	405	405
11	Total heat transmitted		5,222	4,855	4,693	4,622	4,518	4,320
12	Length in kiln required for stage .. .. .. feet		33.1	35.6	36.8	37.4	38.2	40.0

Length required for Stage.—The standard coal required for evaporation and for shell radiation loss in Stage (5) is 2.37 lb. per 100 lb. of clinker ; also the clinker output is 578.5 lb. per minute ; hence

$$\text{Stage length} = \frac{2.37 \times 5.785 \times 12{,}600}{4{,}518} = 38.2 \text{ ft.}$$

Tabulation of Results.

(255) The heat transmission per foot run of kiln and the stage length required have been calculated for cubes ranging from $\frac{1}{8}$ in. to $1\frac{1}{2}$ in. length of side and with a charge of $9\frac{1}{2}$ per cent. The result is shown in Table XXXIX.

Col. (1) shows the heat transmission in Stage (5), also with a $9\frac{1}{2}$ per cent. charge as calculated by the original method, which assumes the lump surface temperature to remain at 212 deg. F. throughout the drying zone. Col. (3), which relates to cubes of $\frac{1}{4}$-in. side, may be taken to represent conditions in the kiln. The average material temperature throughout the heating cycle for $\frac{1}{4}$-in cubes (see Table XXXVIII) is only 218 deg. F., but owing to the rapid rise of the lump surface temperature during the short period of heating on the lower arc the total heat transmission per foot run of kiln, as compared with col. (1), falls off by nearly 10 per cent. as shown in line (11).

Effect of Lump Size.—Comparing in lines (11) and (12) the charge of $\frac{1}{8}$-in. cubes with the charge of $1\frac{1}{2}$-in. cubes, it is seen that the rate of heat transmission to the larger size falls off by 11 per cent. This loss is perhaps less than would be expected. The accuracy of the result depends to a considerable extent on the value used for K ; this is given in Appendix I, line (19).

Summary.

(256) The loss in heat transmission due to the rise of the lump surface temperature when receiving heat on the kiln lining occurs throughout the kiln where the material is dry on the surface. It has been partly, but not sufficiently, allowed for in Stages (6) to (12) [see para. (239) (*b*)]. It would be an improvement in method to take correct account of it in each stage as is done in para. (253). It may then be necessary to increase to some extent some of the emission and absorption factors listed in Table XXVI. The writer accordingly proposes again to review the various kiln tests on which the calculations made in these articles are based, and a statement of the result will be made in a final article.

It may be pointed out, however, that the investigation made in this article confirms the substantial accuracy of the earlier calculations which fix the length of the drying zone at or near 70 per cent. of the length of the kiln, and the improvement in method proposed above would only make a small change in the length of the drying zone, or of the decomposition zone, as calculated for any kiln. It will be realised that measurements of the lump surface temperature would be extremely difficult to make in any stage of the kiln in practice, hence a suitable method of calculation requires to be developed.

APPENDIX I.

HEATING CONDITIONS AT THE CENTRE OF STAGE (5).

(1)	Kiln diameter inside lining .. .. ft.	8.36
(2)	Charge .. .. per cent.	9.50
(3)	Length of upper lining arc .. .. ft.	19.60
(4)	Length of lower lining arc .. .. ,,	6.66
(5)	Length of material chord .. .. ,,	5.98
(6)	Length of lower lining arc per cent. circumference	25.4
(7)	Revolutions of kiln per minute	1.0
(8)	Slope of kiln	1 in 25
(9)	Clinker output .. .. lb. per minute	578.5
(10)	Average gas temperature .. .. deg. Fah.	1,993
(11)	P.D. value for gas radiation .. .. H_2O	1.02
(12)	,, ,, ,, ... CO_2	1.84
(13)	Convection constant H_c. Gas and lining	1.98
(14)	,, ,, ,, Gas and material	2.34
(15)	Rate of heat transfer between lower lining arc and material underside, in Stage (5), expressed in B.T.U. per square foot per hour per deg. Fah. (or H_{con})	22.0
(16)	Density of dry material in frustum LPSO (Fig. 49) expressed in lb. per cubic foot	113
(17)	Specific heat of dry raw material in frustum	0.25
(18)	,, for equivalent block LUVO	0.0729
(19)	Conductivity K of material in frustum LPSO, in B.T.U. per square foot per hour per deg. Fah. per inch thick	3.0
(20)	Time of passage through Stage (5) .. .. minutes	17.4

APPENDIX II.

CALCULATION OF HEATING CYCLE PERIOD.

(257) The preliminary data will be found in Appendix I, lines (1) to (7). A heating cycle period is defined in para. (247).

Let V = charge volume in cubic feet per foot run,
S = side of cube in feet,
N = number of cubes in charge per foot run,
hcP = heating cycle period in minutes,
aL = length of lower arc in feet,
cL = length of material chord in feet,
aT = heating time for any cube on lower arc per cycle (minutes),
cT = heating time on chord per cycle (minutes).

The interstices between the individual cubes are assumed to be 30 per cent. of the charge volume, hence we have $N = \frac{0.7 \times V.}{S^3}$

The number of cubes which are heated on, or from, the lower arc at any instant is $aN = \frac{aL.}{S^2}$ Hence the time required to heat all the cubes for aT minutes is $hcP = \frac{N}{aN} \times aT$.

Substituting values for N, and aN as found above we have

$$hcP = \frac{0.7 \times V}{S} \times \frac{aT}{aL} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

Taking for example cubes of ½-in. side, the value of aT is fixed by the lining speed and by the length of the lower arc at 0.254 minute; also $V = 5.21$, $S = \frac{1}{2}$-in., or $\frac{1}{24}$ft., hence

$$hcP = \frac{0.7 \times 5.21 \times 0.254 \times 24}{6.66} = 3.34 \text{ minutes.}$$

(258) During each heating cycle a cube is heated "on chord" for a definite length of time which is found as follows. The number of cubes heated "on chord" at any instant is $cN = \frac{cL.}{S^2}$ Since there are N cubes, each cube must be heated "on chord" for a time which is given by $cT = \frac{cN}{N} \times hcP$. Putting in values for cN and N as already found we get

$$cT = \frac{cL}{aL} \times aT \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

For cubes of ½-in. side $cT = \frac{5.98}{6.66} \times 0.254 = 0.228$ minute.

It will be noted from formulæ (11) and (12) that the length of a heating cycle varies inversely as the length of the cube side. Also the heating time on the lower arc per heating cycle, and the heating time "on chord," depend on the charge dimensions and on the kiln speed, but not on the cube dimensions.

APPENDIX III.

(259) The heat distribution in the raw material cubes listed in Table XXXVIII has been obtained throughout the heating cycle by the aid of formulæ and graphs in *Industrial Heat Transfer*, by Schack, Goldschmidt, and Partridge, or in *The Calculation of Heat Transmission*, published by the Fuel Research Board. The text books take the case of a parallel bar (see Fig. 48) the sides of which are insulated against gain or loss of heat. The ends AB and CD are suddenly exposed to surroundings of a different temperature, the heat being transferred by radiation or convection. Graphs are provided to show the temperature of the end faces and the temperature of the centre plane of the bar EF after any period of time.

Referring to Fig. 49 it can be shown generally that the temperature difference which would produce a given heat flow from the face LO to the face PS of the frustum of a cube would produce the same flow across a parallel block LUVO, if LU is taken equal to $a^2 \times \left(\frac{1}{2b} - \frac{1}{2a}\right)$ where LO = a and PS = b. In this case $a = 1$ in. and $b = \frac{1}{2}$ in., so that LU = ½ in. Since, however, the volume of the equivalent block is greater than that of the frustum, the specific heat of the former is correspondingly reduced, i.e., from 0.25 to 0.0729. Replacing the frustum by the equivalent block the rise of the surface temperature of the face LO when resting on the kiln lining can be obtained by using the graphs for the parallel bar. The data used in the case of the 1-in. cubes is given in Appendix I, lines (15) to (19), also in para. (249).

(260) The surface temperature of the face LO of the equivalent block being established during the heating period on the kiln lining, the next step is to find the temperature distribution in the interior of the block. The method due to

E. Schmidt is employed, the block being divided into eight parallel strips. The curve AB (Fig. 50) shows the temperature distribution across the block when the face LO enters on to the lining, the gradient being due to the heat supply received " on chord." The temperature distribution across the equivalent block when the face LO leaves the lining is shown by the curve CB. At the end of the diffusion period curve CB again coincides with curve AB, and the heat represented by the area ACB has passed through the block to evaporate moisture at the face UV.

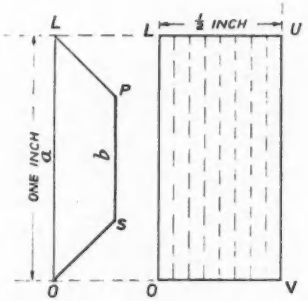


Fig. 49.

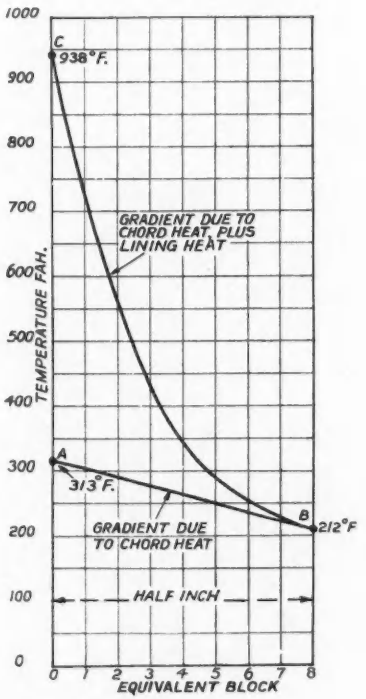


Fig. 50.

(261) LUMP LOSS DUE TO HEAT SUPPLY " ON CHORD."—The heat received by 1 sq. ft. of cube surface during a period of 0.228 minute is 98.9 B.T.U. [see para. (254)]. Since one cube face only is being considered the heat is supplied at intervals throughout a diffusion period of 9.8 minutes. To reach the moist surface it has to pass through the equivalent block, which is ½-in. thick. The heat supplied per square foot of cube surface per hour is $\frac{98.9 \times 60}{9.8} = 605$ B.T.U.

Denoting the temperature difference between the two faces of the equivalent block LUVO by Td, we have $\frac{K \times Td}{\text{thickness in inches}} = 605$. The value of K [see Appendix I, line (19)] is 3.0, hence $Td = \frac{605 \times \frac{1}{2}}{3} = 101$ deg. F.

(262) Starting from the temperature distribution shown by curve CB in Fig. 50 the fall in temperature of the face LO throughout the diffusion period is next obtained by Schmidt's method, due allowance being made for the heat received " on chord." The result is shown by curve LHM in Fig. 47.

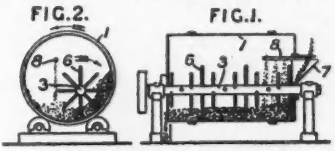
(To be concluded.)

Recent Patent Relating to Cement.

Converting Slurry and Powders into Nodules.

411,446. Fasting, J. S., 9, Monrads Alle, Copenhagen. December 5, 1932.

Pulverulent or slurry-like materials, *e.g.*, raw cement, are converted into nodules by being passed through a rotary drum wherein they are subjected both to tumbling due to the rotation of the drum and to compression by a positively driven member or members in contact with or digging into the material.



Converting Slurry and Powders into Nodules.

Preferably the compression member comprises radial arms on a shaft rotating in the opposite direction to that of the drum. As shown in Figs. 1 and 2, the apparatus comprises a horizontal rotating drum (1) and a rotating compression device comprising an eccentrically mounted shaft (3) having radial arms (6) arranged to dig into the charge of material. The drum and compression device rotate in opposite directions as indicated by the arrows. The material is fed into the drum, through a stationary hopper (7), either with the necessary water content or as a dry powder; in the latter case water is sprayed on to the material from a pipe (8). In a modification, a cylindrical screening device is provided at the outlet end of the drum for separating grains under a certain size, and an outer drum is provided for conveying these small grains back to the hopper. When treating slurry, dry material, such as calcined or partly calcined cement, may be added to the dewatered slurry to prevent sticking. The mixture of dewatered slurry and calcined material may be kneaded in a roller mill before it is fed to the drum.

SITUATION VACANT.

Applications (which will be treated as confidential) are invited for position of Works Manager for Cement Works to be erected in Colonies. Applicant should be capable of taking control of erection of works and have sound knowledge engineering and cement chemistry. State age and salary required. Box No. 1010, " Cement and Cement Manufacture," 20, Dartmouth Street, Westminster, S.W.1.

CEMENT MACHINERY SALES.

QUALIFIED ENGINEER, A.M.I.Mech.E., for ten years successful London Representative of leading Cement Machinery Manufacturer, will be free in May. He is looking for a field where intimate knowledge of the Cement Machinery Market, personal contact with the leading personalities in the Cement Industry of the World, together with visits to almost every European and Asiatic Cement Factory, detailed knowledge of all questions relating to negotiation, finance, estimating, sales, heat economy, erection and starting, as well as common sense, are of real value. Box No. 1009, *Cement and Cement Manufacture*, 20, Dartmouth Street, Westminster, London, S.W.1.

The Analysis of Concrete.

Two well-known firms of cement and concrete testers, Mr. R. H. Harry Stanger and Messrs. Woodcock and Mellersh (late Bertram Blount), both of whose laboratories are in Westminster, have jointly supplied the following :

THE sampling and analysis of concrete presents many difficulties, which must be overcome if the final analysis is to represent the actual composition of the concrete, and the following method describes the way in which these difficulties have been overcome in our laboratories.

As it is common knowledge that the sample must be so taken that it does not contain an excessive proportion of either stones or sand, it is not proposed to make more than a passing reference to this. The methods of preparation of the sample and the methods of analysis differ very considerably. Each chemist usually has his own methods for overcoming these difficulties, and some of these, such as attempting to dissolve a broken lump of concrete or crushing the whole sample to a powder before analysis, introduce other difficulties which are very liable to give erroneous results.

The importance of having a method of analysis which can be accepted as giving results which will represent the actual composition of the concrete has now become urgent, owing to the ever-increasing use of concrete, and we therefore put forward an unpublished method originally drawn up by the late Bertram Blount (of Stanger and Blount) which has given satisfactory results for over thirty years, and has only been modified in a few minor points from time to time in order to bring it into line with modern practice.

The method of preparing the sample retains the stones and sand practically in their original condition, and the complete solution of the cementitious matter in cold dilute acid with a final clearing up, by means of dilute alkali, of any silica previously precipitated from the cementitious matter through carbonation gives results which are very close to the original composition and does not introduce any fresh difficulties or errors. For simplicity we give the description of the method as issued to the chemists in our laboratories, as we think that this will be more generally useful. We, however, do not wish to imply that the success of the method is in any way dependent on the size of dish, filter paper, etc., used by us.

Preparation of Sample.

The sample should be in the form of a solid lump and should be large enough to be representative. In the case of normal aggregates a 6in. cube is very convenient, but the presence of a proportion of 2in. aggregate would necessitate a somewhat larger sample. If the sample is cut out from work, an approximate 6in. cube should be aimed at. It is very dangerous to pick up a number of pieces cut out with a chisel and lump them together as a representative sample, and still worse to collect the rubble removed.

By far the best method of breaking is to compress the sample in a testing machine to the point of complete breakdown. In some cases the solid " cores "

may be freed from weakened concrete and kept in reserve, and the whole of the shattered portion used for the analysis. The weakened sample is broken up by hand as far as possible, and then rubbed in a large Wedgwood mortar using a rolling action in such a manner as to avoid breaking stones. Large stones are removed by hand and cleaned as far as possible by light chipping with a ¼in. cold chisel. From time to time the contents of the mortar are transferred to a ⅛in. mesh sieve and the fine material eliminated. By this means it is possible to divide the sample into two major portions—stones larger than ⅛in. mesh, comparatively free from mortar, and "fine stuff" passing the sieve. It is very important that mortar nodules should not be allowed to remain with the stones, but attached mortar is normally small in percentage and is allowed for later. In the case of many concretes a skilful operator will soon be able to carry through this sampling operation in three hours or so.

The "fine stuff" and the contaminated stones are then weighed separately and a representative, well-mixed sample of the former is bottled for the analyst. The stones are then placed in a large shallow dish (a large photographic enlarging dish is very suitable) and covered with a 7 per cent. solution of hydrochloric acid (7 c.c. concentrated acid per 100 c.c.). If any pieces of limestone are observed they should be rapidly removed and washed. The stones are allowed to remain in contact with the acid for 24 hours and the latter is then carefully poured off, the stones washed several times, and finally dried. They are then transferred to an ⅛in. mesh sieve and the residue retained is weighed. The difference between this weight and the original weight of the contaminated stones is added to the weight recorded for "fine stuff." It should not normally exceed 1 per cent. of the total weight of fine stuff.

At this stage the recorded figures will be as follows:

Weight of contaminated stones	A
,, ,, clean stones	B
,, ,, fine stuff	C
True weight of fine stuff	C + A − B
Total weight of sample	A + C

Analysis of Fine Stuff.

Ten grammes, without any further grinding, are placed in a 6in. porcelain dish and 200 c.c. of 10 per cent. hydrochloric acid (10 c.c. of concentrated acid per 100 c.c.) are added. The dish is covered with a 7in. clock glass and allowed to stand for 15 minutes at room temperature, with occasional stirring by means of a bent glass rod kept hanging in the lip of the dish. The liquid is then carefully decanted through an 11-cm. filter into a 500-c.c. measuring flask. When the bulk of the acid liquor has been transferred, the residue is gently crushed with the glass rod until any possible "cores" have been broken down and gelatinous silica has been detached from the sand as far as possible. A further 100 c.c. of 7 per cent. hydrochloric acid are then added and the dish is covered and allowed to stand for at least two hours with occasional stirring. The bulk of the solution is again decanted through the filter and the residue is washed with several

25-c.c. portions of 7 per cent. hydrochloric acid and finally with cold distilled water until both residue and filter are free from soluble chlorides. The residue on the filter is then washed back into the dish and the whole digested for 15 minutes, covered, just short of boiling, with 100 c.c. of a freshly prepared 10 per cent. sodium carbonate solution (270 grammes of crystals to 1,000 c.c. of water). The same filter is now placed over a 250-c.c. flask and the sodium carbonate liquor is decanted through it. The residue in the dish and filter is washed with several further 25-c.c. portions of hot sodium carbonate solution and the filtered solution is cooled and bulked to 250 c.c. The funnel is then placed over a beaker and both it and the residue in the dish are washed with acidified water until free from alkali, and finally with water until no acid remains. In this way there is little danger of the filter becoming clogged with colloidal clay. The whole of the insoluble matter is washed into a weighed dish, evaporated to dryness, dried at 105 deg. C. and weighed. If it is desired to separate clayey matter from sand it should be done at this stage, prior to drying. The filter is ignited and the weight of the ash added to the main sand weight.

An aliquot portion, say 50 c.c. of the sodium carbonate liquor, is acidified with hydrochloric acid in a covered dish and then evaporated to dryness, baked, and the silica determined as described later. This is usually designated as " recovered silica."

The original acid filtrate is bulked to 500 c.c. and analysed as follows.

Main Bases.

100 c.c. are evaporated to dryness in a 6in. shallow pattern porcelain dish. It is essential that the dish is of such shape that the residue on evaporation is distributed in the form of a thin layer over a considerable area. The dish is then covered and baked over an electric- or gas-heated hotplate to a temperature of approximately 200 deg. C. and not exceeding 250 deg. C. After baking, and immediately it is cool enough, the residue is digested for five minutes with 30 c.c. of concentrated hydrochloric acid, diluted to 60 c.c. and filtered at once through a good filter (9 or 11 c.m.) carefully washing with hot water (five washes are usually sufficient). If the residue is allowed to deliquesce before the addition of the acid, or the filtration is unduly prolonged, low results will be recorded for silica and the R_2O_3 precipitate will be contaminated. The silicic acid adhering to the dish is not scrubbed on until the washing is complete, as filtration becomes slow if it is treated in the normal manner. The volume of wash water in the final operation is kept as low as possible.

As soon as washing is complete the filtrate is treated with a few drops of a saturated solution of bromine in hydrochloric acid and a slight excess of ammonia in a 6in. porcelain dish. It is then digested just short of boiling point, uncovered, until only a faint smell of excess ammonia remains. The precipitated hydroxides of iron, alumina, and manganese are filtered off through a 15-cm. filter in a fluted funnel, scrubbed on, and washed with hot water (five washes are usually sufficient). The filtrate is rendered distinctly ammoniacal again by the addition of 10 c.c. of ammonia (1 part 0.880 to 1 part water) and brought to the

boil. Whilst still boiling, 50 c.c. of saturated ammonium oxalate solution, also at boiling point, are added and the whole is boiled for one minute. The precipitated calcium oxalate is allowed to stand for at least two hours and filtered through a 15-cm. paper in a fluted funnel, washing as usual. The filtrate is placed in a 6in. porcelain dish (we have found State Berlin to be safest) and evaporated over a solid flame burner until crystallisation commences, 40 c.c. of concentrated nitric acid are added, the dish covered immediately, and the liquid evaporated over a low flame with the cover still on until all ammonium salts have been destroyed and a clean dry white residue is left in the dish. This residue is taken up in 2 c.c. of concentrated HCl and a little hot water, rendered ammoniacal, two drops of saturated ammonium oxalate solution are added and the whole is digested until just faintly ammoniacal. The small precipitate so formed is filtered off through a 7-cm. filter, well washed, and rejected. This consists mainly of silica, etc. picked up from glass vessels, but contains a maximum of 1 mgm. of calcium oxalate, which escaped precipitation previously on account of its solubility. This must be determined in the case of very accurate work. The object of removing it at this stage is to prevent contamination of the magnesium precipitate. The filtrate, which should not exceed 100 c.c. in bulk, is rendered distinctly ammoniacal and magnesia is precipitated by the addition of sodium phosphate as usual. After the addition of the latter reagent, the beaker is well shaken intermittently during one hour. The crystalline precipitate should have settled out quite cleanly by this time and is allowed to stand for a further hour, filtered off through a 9-cm. paper, and well washed with dilute ammonia (1 part 0.880 to 10 parts water).

Treatment of Precipitates.

The silica is partially dried and transferred to a platinum crucible, and the R_2O_3 precipitate is treated similarly. The calcium oxalate is almost completely dried and transferred to a weighed platinum crucible. These three precipitates are first burnt off at the mouth of a muffle furnace until free from carbon and then ignited to a temperature of 1,100 deg. C. for one hour. We have found this temperature to be essential for the complete decomposition of the calcium carbonate ; the muffle cavity also should be ventilated. The precipitates are weighed in their crucibles after cooling in a good desiccator for not less than 15 minutes, and not more than 30 minutes. The magnesia precipitate is partially dried, and ignited over a good burner in a weighed porcelain crucible.

Determination of Iron.

This is carried out on a 100 c.c. of the original solution by any recognised method.

Determination of Sulphuric Anhydride.

100 c.c. of the original solution are boiled and treated with barium chloride as usual.

Carbonic Anhydride.

This is determined on 5 grammes of the fine stuff by treatment with dilute hydrochloric acid and absorption in potash as usual.

Interpretation of Results.

The results may now be tabulated as follows :

Clean stones	per cent. by weight
Total fine stuff	" " "
	100.0

Analysis of " Fine Stuff."

	Per cent. by weight	
Insoluble residue (sand)		
Fine silt and clay (if determined) ..		
Soluble silica		Total cement silica
Recovered silica		Total cement silica
Alumina (and manganese)		
Ferric oxide		
Calcium oxide		
Magnesia		
Sulphuric anhydride		
Carbonic anhydride		
Combined water, etc. (by difference) ..		
	100.0	

The first step is to calculate back the main analysis as percentage by weight of the concrete. The percentage composition of the " cement " is then calculated from the total cement silica, alumina, ferric oxide, calcium oxide, magnesia, and sulphuric anhydride. This should agree reasonably with the composition of anhydrous Portland cement. The most usual discrepancy is a high figure for ferric oxide with corresponding reduction of the other figures. If this occurs sufficient of the R_2O_3 content should be deducted and considered as aggregate to rectify the analysis. The true cement content will then be the original total minus this correction, an addition of 1 per cent. being made for combined water. If the analysis has been carefully carried out this correction will be a small proportion of the cement content, and the final cement analysis will be found to agree closely with the composition of the original cement.

If the carbonic anhydride content is more than 1 per cent. or so it will be necessary to detach a portion of the lime and transfer it to the aggregate as calcium carbonate. If this is necessary the deduction will correct what may at first appear to be a discrepancy in the cement analysis.

Finally, it must be pointed out that this method is only applicable to aggregates composed of ballast, insoluble granite, etc., where the calcium carbonate content is less than 10 per cent. Limestone aggregate, coke breeze, aluminous cement, etc., all give rise to complications, but we have always found that a modification of the above method gave the best results even in the most difficult cases, and if it is necessary to crush down a sample completely, as in the case of limestone, it should only be crushed so far that it passes a $\frac{1}{16}$ in. mesh sieve, for

solution of a considerable proportion of silica from the aggregate will be found to take place when the analysis of a finely powdered mixture is attempted. This does not apply, of course, if no silica sand has been used, but such is not usually the case.

Proposed New System of Cement Testing.

We have received the following from Mr. A. B. Searle on the points raised by Dr. Platzmann in the article entitled "A New System of Cement Testing," published in our March issue.

Dr. Platzmann's article interests me greatly because, as a chemist, I have for many years considered that far more attention should be paid to the evaluation of cement on the basis of a series of chemical tests as soon as sufficient data is available. This now appears to be the case, and an opportunity should be sought for changing the basis of specification accordingly. At the same time I am in favour of retaining some physical tests, such as those for setting time and soundness and for the crushing strength. The tensile strength test is an old inheritance and should have been abandoned twenty years ago for reasons familiar to all who are interested in testing cements.

There should not be any insuperable difficulty in securing an international agreement to embody in an International Specification—

(i) A mineralogical analysis showing the proportion of each mineral present.

(ii) A statement of the conclusions to be derived therefrom relative to the properties of the cement.

(iii) A statement of the setting time.

(iv) A statement of the minimum hardening time sufficient to permit the concrete to be used for general purposes.

(v) A soundness test.

(vi) A minimum crushing strength which should be such that it enables either hand-tamping or mechanical tamping to be used.

(vii) A limit for the heat of hydration, possibly to be applied only to cement to be used for mass concrete.

There is only one serious objection to these tests, namely their cost, but this appears to be unavoidable. The present physical tests are cheap, but they are by no means as comprehensive as they should be and there is a danger of their creating a sense of security which is liable to be misleading.

A standard specification can only relate to cement of minimum quality which can be used with safety for general purposes. Users will naturally impose their own more stringent specifications when the cement is to be used for special purposes, or where unusual properties are required. As cements having different properties will necessarily be required for some purposes, it seems to complicate the matter needlessly to have several standard Specifications although theoretically this suggestion is perfectly sound. On the whole, however, it seems more practicable to let the standard specification be a general one, leaving users free to modify it for their special requirements.

The Effects of Fluorides on Thermal Synthesis of Calcium Aluminates and Calcium Silicates.

By SHOICHIRO NAGAI and TOYOTARA YOSHIURA.

Calcium Aluminates.

IN the course of a paper presented to the Japanese Society of Chemical Industry, the authors state:

There is very little information available on the effects of calcium fluoride and other fluorides on the thermal synthesis of calcium aluminates, which are the main hydraulic compounds of Portland cement and high alumina cement. Mr. Nagai, in co-operation with M. Miyasaka, has recently reported studies on the effects of calcium fluoride on the thermal synthesis of calcium silicates* and is now continuing the studies. The effects of calcium fluoride on the thermal synthesis of calcium aluminates are now being studied by the same method, and the following are the main points of the first report.

The raw mixtures were made from the pure chemicals—calcium carbonate, alumina, calcium fluoride, etc.—in the molecular ratios of (1) $3CaCO_3 : Al_2O_3$(3 : 1) or $3CaO : Al_2O_3$(3 : 1), (2) $5CaCO_3 : 3Al_2O_3$(5 : 3) or $5CaO : 3Al_2O_3$(5 : 3), (3) $CaCO_3 : Al_2O_3$(1 : 1) or $CaO : Al_2O_3$(1 : 1), and (4) $3CaCO_3 : 5Al_2O_3$(3 : 5) or $3CaO : 5Al_2O_3$(3 : 5). These mixtures were heated, with or without calcium fluoride, in a tube furnace. The conditions of heating time, temperature, etc., were strictly regulated in each case. The amount of calcium fluoride in the raw mixtures was 1 per cent. of the mixtures, and other percentages, 0.25, 0.50, 2.0, 3.0, 5.0, etc., were also compared in some cases. The heated products were tested systematically on the degree of combination between CaO and Al_2O_3 in the following sequence: (1) free lime or uncombined lime, (2) insoluble residue, or uncombined or free alumina, (3) total lime, (4) total alumina, (5) combined lime from (3)–(1) and its percentage, (6) combined silica from (4)–(2) and its percentage, (7) amount of synthesised calcium aluminates, (8) molecular ratio of combined lime to combined alumina or molecular ratio of lime to alumina of the synthesised calcium aluminates, (9) amount of calcium fluoride remained in the heated products and its percentage.

Some results are given in the following tables, from which it is seen that the addition of 1 per cent. calcium fluoride has a decided effect on the formation of calcium aluminates in the following points: (1) comparing the same degree of formation of calcium aluminates, the addition of 1 per cent. calcium fluoride lowers the heating temperature by about 150 to 200 deg. C. (2) The combination of lime proceeds faster than that of alumina. The molecular ratio of lime to alumina becomes a little greater and nearly 1.67 of the aluminate $5CaO : 3Al_2O_3$

* *Cement and Cement Manufacture*, October, 1934.

TABLE I.

COMPARISON OF SYNTHESIS OF CALCIUM ALUMINATE FROM MIXTURE $3CaCO_3$:Al_2O_3(3 : 1) WITH AND WITHOUT CALCIUM FLUORIDE (1 PER CENT.). HEATING TIME 1 HOUR.

No. of Exp.	Heating Conditions. Temperature.	CaF_2.				CaO.			Al_2O_3.			Total amount of calcium aluminates.	Molecular ratio of CaO:Al_2O_3.
		Added.	Theoretical amount in heated product.	Remained.	Percentage.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	°C.	%	%	%	%	%	%	%	%	%	%	%	
CA_{3102}	1000	0	0	0	0	59.95	2.45	3.96	33.06	4.60	12.21	7.05	0.97 : 1.00
CA_{3104}	1200	0	0	0	0	46.70	15.54	24.98	16.20	21.54	57.10	37.08	1.31 : 1.00
CA_{3106}	1400	0	0	0	0	20.66	41.49	66.80	1.99	35.81	94.72	77.30	2.21 : 1.00
CAF_{31102}	1000	1	1.49	0.89	59.7	51.41	10.37	16.61	18.38	19.16	51.02	29.53	0.99 : 1.00
CAF_{31104}	1200	1	1.49	0.74	49.7	37.70	24.24	38.85	4.93	32.52	86.90	56.76	1.36 : 1.00
CAF_{31106}	1400	1	1.49	0.63	42.6	17.13	44.92	71.87	0.76	36.80	98.00	81.72	2.21 : 1.00

even at about 1,300 deg. C. The remaining calcium fluoride becomes gradually smaller at higher heating temperatures, showing easier vaporisation than in the case of calcium silicates.

The combination test was carried out by changing the heating time from 0.5 hour to 1, 2 and 3 hours, with or without calcium fluoride, and the results in Table II were obtained. From these results it is seen that the combination

TABLE II.

COMPARISON OF SYNTHESIS OF CALCIUM ALUMINATES FROM MIXTURE $3CaCO_3$:Al_2O_3(3 : 1) WITH OR WITHOUT CALCIUM FLUORIDE (1 PER CENT.) BY HEATING AT 1,300° C. FOR 1 TO 3 HOURS.

No. of Exp.	Heating condition.		CaF_2.			CaO.			Al_2O_3.			Total amount of calcium aluminates.	Molecular ratio of CaO:Al_2O_3.
	Temperature.	Time.	Added.	Theoretical amount in heated product.	Remained.	Percentage.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	°C.	hr.	%	%	%	%	%	%	%	%	%	%	%	
CA_{3105}	1300	1	0	0	0	0	40.46	21.80	35.02	10.12	27.58	73.13	49.38	1.44 : 1.00
CA_{3111}	1300	2	0	0	0	0	36.41	25.92	41.60	5.57	32.07	85.20	57.99	1.47 : 1.00
CA_{3112}	1300	3	0	0	0	0	28.69	33.63	54.00	3.41	34.34	91.00	67.97	1.78 : 1.00
CAF_{31105}	1300	1	1	1.49	0.71	47.6	31.57	30.37	48.62	2.95	34.56	92.16	64.93	1.60 : 1.00
CAF_{31111}	1300	2	1	1.49	0.70	47.0	28.11	33.87	54.20	2.45	35.05	93.50	68.92	1.76 : 1.00
CAF_{31112}	1300	3	1	1.49	0.65	43.6	26.50	35.49	56.81	1.85	35.67	95.15	77.16	1.82 : 1.00

between lime and alumina is considerably promoted by the presence of 1 per cent. calcium fluoride, but longer heating is not so effective even with the presence of calcium fluoride.

Further studies on the effect of different amounts of calcium fluoride (0.25, 0.5, 1.0 and 2.0 per cent.) were carried out and the results given in Table III were obtained. It is clear from these results that the more calcium fluoride

TABLE III.

COMPARISON OF SYNTHESIS OF CALCIUM ALUMINATES FROM MIXTURE $3CaCO_3:Al_2O_3(3:1)$ WITH DIFFERENT AMOUNTS OF CALCIUM FLUORIDE 0.5 TO 2.0 PER CENT. BY HEATING AT 1,300° C. FOR 1 HOUR.

No. of Exp.	CaF_2.				CaO.			Al_2O_3.			Total amount of calcium aluminates.	Molecular ratio of $CaO:Al_2O_3$.
	Added.	Theoretical amount in heated product.	Remained.	Percentage.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	%	%	%	%	%	%	%	%	%	%	%	
CAF_{31050}	0.5	0.75	0.42	56.0	32.08	30.03	48.55	2.16	32.40	94.30	65.43	1.56 : 1.00
CAF_{31105}	1	1.49	0.71	47.6	31.57	30.37	48.62	2.95	34.56	92.16	64.93	1.60 : 1.00
CAF_{31200}	2	2.99	0.78	26.1	30.91	31.35	49.90	2.01	35.13	94.59	66.48	1.63 : 1.00

added the more the amount of vaporisation increases; the amount of produced calcium aluminates and the molecular ratio of lime to alumina increase very slightly, owing to the amount of remaining effective calcium fluoride.

Further studies on the mixtures $5CaCO_3 : 3Al_2O_3(5:3)$, $CaCO_3 : Al_2O_3(1:1)$, and $3CaCO_3 : 5Al_2O_3(3:5)$, with and without calcium fluoride or other fluorine compounds, are being carried on.

Calcium Silicates.

A systematic study is reported on the effects of adding calcium fluoride on the thermal synthesis of tricalcium silicate, $3CaO.SiO_2$, from the mixture $3CaCO_3 : SiO_2(3:1)$.

The mixture $3CaCO_3 : SiO_2(3:1)$ or $3CaO : SiO_2(3:1)$ was heated with and without calcium fluoride. The heating time, temperature, analytical method of the products, etc., were strictly regulated. The amount of calcium fluoride mainly studied was 1 per cent. of the mixture $3CaCO_3 : SiO_2(3:1)$. Other percentages (0.25, 0.50, 2.0, 5.0 per cent., etc.) were also compared for their effects on the preparation of $3CaO.SiO_2$ by changing the heating time and the temperature.

The heated products were tested for the degree of combination between CaO and SiO_2 effected by the added calcium fluoride as follows: (*a*) free lime or uncombined lime, (*b*) insoluble residue or uncombined or free silica, (*c*) total lime, (*d*) combined silica or soluble silica, (*e*) combined lime from (*c*) − (*a*), (*f*) amount of synthesised calcium silicate from (*e*) + (*d*), (*g*) ratio of combined lime to combined silica from (*e*) − (*d*), (*h*) molecular ratio of combined lime to combined silica from 1.07 × (*g*), (*i*) amount of calcium fluoride retained in the heated products, (*j*) percentage of retained calcium fluoride to the theoretical amount of the fluoride added.

Some of the results are compared in Table IV. It can be seen that the addition of calcium fluoride (1 per cent.) has a considerable effect on the combination of lime and silica to tricalcium silicate $3CaO.SiO_2$ even at 1,300 deg. C. According to the previous studies by S. Nagai and K. Akiyama and by K. Murakami, $3CaO.SiO_2$ could not be synthesised by heating only even at

1,400 to 1,450 deg. C. from the mixture $3CaCO_3 : SiO_3(3 : 1)$ without CaF_2. The addition of only 1 per cent. of CaF_2 produces $3CaO.SiO_2$ very easily even at 1,300 deg. C.

TABLE IV.

COMPARATIVE RESULTS OF SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $3CaCO_3:SiO_2(3:1)$ WITH OR WITHOUT CALCIUM FLUORIDE (1 PER CENT.).

No. of Exp.	Heating Temperature.	CaF_2.		CaO.			SiO_2.			Amount of calcium silicates.	Molecular ratio of $CaO:SiO_2$.
		Added	Remained.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	°C.	%	%	%	%	%	%	%	%	%	
CS_{3102}	1200	0	0	44.66	28.86	39.24	8.89	17.65	66.52	56.51	1.75 : 1.00
CS_{3104}	1400	0	0	30.81	43.10	58.26	3.91	22.49	85.21	65.59	2.05 : 1.00
CSF_{31102}	1200	1	1.15	33.12	40.16	54.18	4.43	21.14	82.75	61.32	2.00 : 1.00
CSF_{31104}	1400	1	1.17	8.18	65.07	87.65	2.07	23.21	89.62	88.28	2.99 : 1.00

The time of heating was 1 hour in the above experiments. The comparison was carried on by changing the reacting time from 1 to 2 hours at 1,200 deg. C., with and without calcium fluoride (1 per cent.). The results are shown in Table V. The temperature of heating was 1,200 deg. C. in each case. These results show

TABLE V.

COMPARISON OF SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $3CaCO_3:SiO_2(3 : 1)$ WITH OR WITHOUT CALCIUM FLUORIDE (1 PER CENT.) BY HEATING AT 1,200° C. FOR 1 AND 2 HOURS.

No. of Exp.	Heating time.	CaF_2.		CaO.			SiO_2.			Amount of calcium silicates.	Molecular ratio of $CaO:SiO_2$.
		Added.	Remained.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	hr.	%	%	%	%	%	%	%	%	%	
CS_{3102}	1	0	0	44.66	28.79	39.18	8.89	17.61	66.46	46.30	1.74 : 1.00
CS_{3106}	2	0	0	39.13	34.69	51.82	6.42	20.21	75.95	54.90	1.83 : 1.00
CSF_{31102}	1	1	1.15	33.12	40.16	54.18	4.43	21.14	82.70	61.30	2.00 : 1.00
CSF_{31106}	2	1	1.43	31.94	40.90	55.13	3.43	22.00	86.46	62.90	1.98 : 1.00

that the combination between lime and silica is not much promoted by longer heating even with 1 per cent. of calcium fluoride at 1,200 deg. C., so that the heating temperature must be higher than 1,250 to 1,300 deg. C. to obtain $3CaO.SiO_2$.

SUPER REFRACTORIES for CEMENT KILNS

ALITE No. 1. 68% ALUMINA
Refractory Standard 3250° Fahr.

ALITE B. 57% ALUMINA
Refractory Standard 3180° Fahr.

ALITE D. 41% ALUMINA
Refractory Standard 3150° Fahr.

E. J. & J. PEARSON, LTD.,
STOURBRIDGE, ENG.

The experiments were further carried on to study on the effects of different amounts of calcium fluoride (1.00 and 2.00). The results are shown in Table VI. The heating temperature of 1,200 deg. C. is not sufficient to obtain $3CaO.SiO_2$ from the mixture, ($3CaCO_3 : SiO_2(3 : 1)$), even with 1 to 2 per cent. of calcium fluoride. The temperature must be higher than 1,250 deg. C., which is well in accord with the results given in Table V. Comparative tests by heating at higher temperatures (1,250 to 1,300 deg. C.) will be carried out later.

TABLE VI.

COMPARISON OF SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $3CaCO_3:SiO_2(3 : 1)$ WITH DIFFERENT AMOUNTS OF CALCIUM FLUORIDE (0.5 TO 2.0 PER CENT.) BY HEATING AT 1,200° C. AND FOR 1 HOUR.

No. of Exp.	CaF_2.			CaO.			SiO_2.			Amount of calcium silicates.	Molecular ratio of $CaO:SiO_2$.
	Added.	Remained.	Percentage.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
	%	%	%	%	%	%	%	%	%	%	
CS_{3102}	0	0	0	44.66	28.79	39.18	8.89	17.61	66.46	46.30	1.74 : 1.00
CSF_{31102}	1.00	1.15	73.8	33.12	40.16	54.18	4.43	21.14	82.70	61.30	2.00 : 1.00
CSF_{31110}	2.00	2.10	67.7	28.35	44.54	59.95	2.75	23.56	89.55	70.85	2.02 : 1.00

In cement manufacturing practice it is commonly believed that the fluoride added to the raw mixture is volatilised by the burning and the clinker does not contain any fluoride. The authors have ascertained that 70 to 80 per cent. of the added fluoride is always retained in the products by heating even at 1,300 deg. C. for 3 to 5 hours, but in the practical rotary kiln the burned gas contains much water and the temperature is a little higher than 1,400 deg. C. To study this point the authors compared the dry thermal synthesis with the wet thermal or so-called hydrothermal synthesis. The results are shown in Table VII. From

TABLE VII.

COMPARISON OF DRY THERMAL AND HYDROTHERMAL SYNTHESES OF CALCIUM SILICATES FROM MIXTURES (a)$CaCO_3:SiO_2(1 : 1)$ AND $2CaCO_3\text{-}SiO_2(2 : 1)$ WITH OR WITHOUT CALCIUM FLUORIDE BY HEATING AT 1,100° C. OR 1,200° C. FOR 1 HOUR.

No. of Exp.	Heating method.	Heating temperature.	Heating time.	CaF_2.			CaO.			SiO_2.			Amount of calcium silicates.	Molecular ratio of $CaO:SiO_2$.
				Added.	Remained.	Percentage.	Free.	Combined.	Percentage.	Free.	Combined.	Percentage.		
		°C.	hr.	%	%	%	%	%	%	%	%	%	%	
CS_{1104}	Dry	1100	1	0	0	0	16.15	31.49	66.03	35.92	16.78	31.83	48.27	1.99 : 1.00
CSF_{11104}	,,	1100	1	1	1.10	80.3	4.36	43.93	89.78	29.02	23.36	44.64	67.29	2.01 : 1.00
$CSFH_{1111}$	Wet	1100	1	1	0.89	64.9	0	48.99	98.72	28.46	21.99	43.56	70.98	2.38 : 1.00
CS_{2104}	Dry	1200	1	0	0	0	32.26	31.92	49.78	15.18	19.71	56.76	51.63	1.73 : 1.00
CSF_{21104}	,,	1200	1	1	1.39	92.9	17.40	46.38	71.50	8.29	26.27	76.42	72.65	1.89 : 1.00
$CSFH_{2111}$	Wet	1200	1	1	0.56	53.3	16.46	48.63	73.26	7.60	26.68	78.10	75.31	1.95 : 1.00

these results it is seen that fluoride retained in the dry heated products was about 70 to 80 per cent., which is twice as large as that retained in the hydrothermally heated products. The problem of the distribution of fluoride will be further studied and reported later.